

An Investigation of Some Free Energies of  
Absorption

By

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## INTRODUCTION

The wetting of solids is a phenomenon of great natural and industrial importance. The spreading of a lubricant over a surface to be lubricated and the spreading and adhesion of paints and protective coatings are all dependent upon this phenomenon. Other illustrations include waterproofing of fabrics, printing, and the process of washing with soaps.

In this paper an inquiry is made to determine the correlation of heats of wetting as measured with a calorimeter and free energy changes calculated from isotherm data. The interaction of various liquids with hydrophilic solids is considered from such data as is available in the chemical literature.



## HEATS OF WETTING

When a solid is immersed in a liquid and physical adsorption occurs, the resulting decrease in surface energy may be measured by a sensitive calorimeter [1]. Although heats of immersion are actually measured, it is customary to define heats of emersion and this practice will be followed here.

The total surface energy ( $E_S$ ), or enthalpy, ( $H_S$ ), of a clean, non-porous solid prior to immersion is given by

$$H_S = \sum_S \left[ \gamma_S - T \left( \frac{\partial \gamma_S}{\partial T} \right)_P \right] \quad (1)$$

where  $\sum_S$  is the area of the solid and  $\gamma_S$  is its surface tension or free surface energy. On immersion in a liquid the solid surface is replaced by a solid - liquid interface with an enthalpy, ( $H_{SL}$ ), which is defined as

$$H_{SL} = \sum_{SL} \left[ \gamma_{SL} - T \left( \frac{\partial \gamma_{SL}}{\partial T} \right)_P \right] \quad (2)$$

The subscripts refer to the interface. If the areas are equal,

$\sum_S = \sum_{SL}$ , and the enthalpy of emersion, ( $H_{E(SL)}$ ), is

$$H_{E(SL)} = H_S - H_{SL} = \sum \left[ \gamma_S - \gamma_{SL} - T \left( \frac{\partial \gamma_S}{\partial T} - \frac{\partial \gamma_{SL}}{\partial T} \right)_P \right] \quad (3)$$

or per unit area

$$h_{E(SL)} = \frac{H_{E(SL)}}{\sum} = \gamma_S - \gamma_{SL} - T \left( \frac{\partial \gamma_S}{\partial T} - \frac{\partial \gamma_{SL}}{\partial T} \right)_{P, \sum} \quad (4)$$



The change in enthalpy is related to changes in internal energy by the equation

$$\Delta h = \Delta \epsilon + \Delta p v$$

or at constant pressure

$$\Delta h = \Delta \epsilon + p \Delta v .$$

Since  $\Delta v$  is small and cannot be detected within the limits of experimental error,

$$\Delta h = \Delta \epsilon .$$

The energy of adhesion,  $\epsilon_{A(SL)}$ , is the change in internal energy when a liquid is separated from a solid at their interface to give clean surfaces of both. The energy of adhesion is given by

$$\epsilon_{A(SL)} = \epsilon_S - \epsilon_{SL} + \epsilon_L = \epsilon_E + \epsilon_L \quad (5)$$

where  $\epsilon_S$ ,  $\epsilon_{SL}$ , and  $\epsilon_L$  refer to the internal energies of the solid, interface and liquid respectively.  $\epsilon_E$  is the internal energy of emersion and since  $h = \epsilon$  it may be seen that the energy of adhesion is simply equal to the heat of emersion,  $h_E$ , plus the surface energy of the liquid. This latter quantity is obtained from the surface tension and the temperature variation of the surface tension of the liquid.

If the solid is no longer clean (that is, if a film is adsorbed on the surface) the free surface energy changes from  $\gamma_S$  to some lower value  $\gamma_{Sf}$  and the total surface energy from



$$h_S = \gamma_S - T \left( \frac{\partial \gamma_S}{\partial T} \right)_{P, \Sigma}$$

to

$$h_{Sf} = \gamma_{Sf} - T \left( \frac{\partial \gamma_{Sf}}{\partial T} \right)_{P, \Sigma} .$$

The enthalpy of emersion,  $h_{E(SfL)}$ , per unit area of solid containing adsorbed molecules is given by

$$h_{E(SfL)} = h_{Sf} - h_{SL} = \gamma_{Sf} - \gamma_{SL} - T \left( \frac{\gamma_{Sf}}{T} - \frac{\gamma_{SL}}{T} \right)_{P, \Sigma} . \quad (6)$$

The following processes, (Fig. 1), define the heat of desorption,  $h_{D(VSf)}$ , and establish the relationship between the heat of desorption and the heat of emersion:

(A.) A solid is emersed from  $n_1$  moles of liquid into a vacuum. Here,  $n_1$  is assumed to be large compared with the  $n$  moles considered in the next step.

$$\Delta H = h_{E(SL)} \quad (7)$$

(B.) The solid is emersed from  $n_1$  moles of liquid into the vapor of the liquid at the pressure  $p_1$  carrying with it a film of just the correct thickness to give it equilibrium with the vapor at this pressure. The amount of liquid removed in this film is  $n$  moles.

$$\Delta H = h_{E(SfL)} \quad (8)$$

(C.) Of the  $n_1$  moles of liquid left in (A.) evaporate  $n$  moles with heat of evaporation,  $\lambda$ , leaving  $(n_1 - n)$  moles, which is the



STEP D  
Equivalent Process

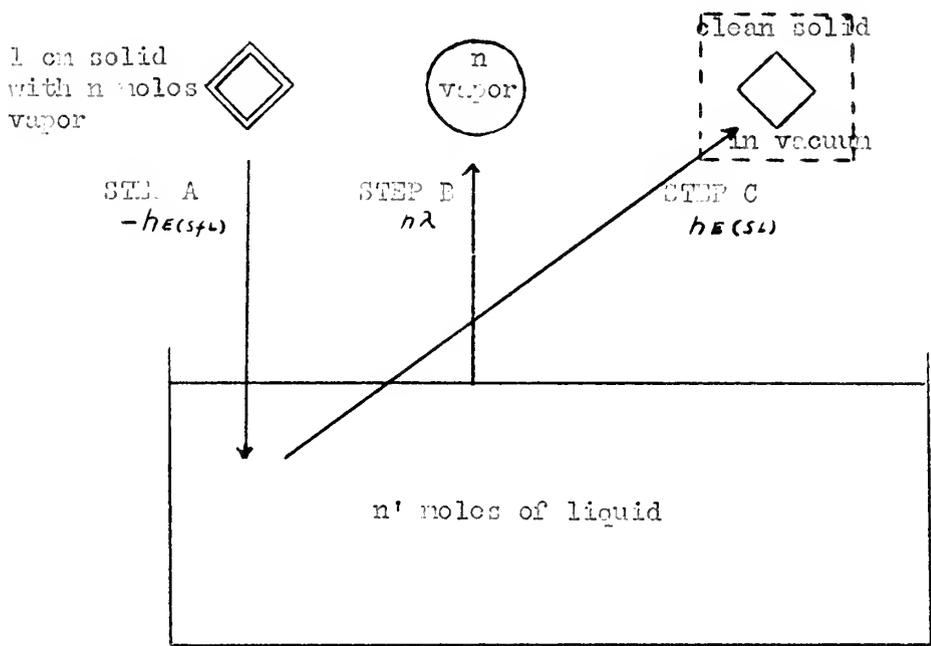


FIG. 1



amount of liquid left in (B.).

$$\Delta H = n\lambda \quad (9)$$

(D.) Subtract equation (8) from the sum of equations (7) and (9), since this will give the increase in the value of the heat function when the film of  $n$  moles is vaporized from the surface of the solid.

The heat of desorption,  $h_{D(VSf)}$ , then is

$$h_{D(VSf)} = h_{E(SL)} - h_{E(SfL)} + n\lambda \quad (10)$$

By substituting equations (1) and (6) for  $h_{E(SL)}$  and  $h_{E(SfL)}$  in equation (10) the heat of desorption is found to be

$$h_{D(VSf)} = \gamma_S - \gamma_{Sf} - T \left( \frac{\partial \gamma_S}{\partial T} - \frac{\partial \gamma_{Sf}}{\partial T} \right)_{P, \Sigma} + n\lambda \quad (11)$$

The heats of desorption may be expressed in calories per gram, calories per mole, or as calories per unit area of the surface of the solid.

From the relation,  $\Delta H = \Delta F - T\Delta S$ , the corresponding free energy terms for a surface and solid-liquid interface are found. The free energy of emersion,  $f_e$ , is defined as

$$f_e = \gamma_S - \gamma_{SL} \quad (12)$$

The work of adhesion,  $W_{A(SL)}$ , for a solid and a liquid is defined as

$$W_{A(SL)} = \gamma_S - \gamma_{SL} + \gamma_L \quad (13)$$



The spreading pressure,  $\pi_e$ , is defined as

$$\pi_e = \gamma_S - \gamma_{SL} - \gamma_L \quad . \quad (14)$$



FREE ENERGY OF ADSORPTION

The Gibbs  $\int$  function is defined as

$$\int = E_{S_0} - T S_{S_0} - \mu_1 \Gamma_1 - \mu_2 \Gamma_2 \quad (15)$$

where  $E_{S_0}$  is the total surface energy,  $S_{S_0}$  is the surface entropy,  $\Gamma_i$  is the surface density of species  $i$ , and  $\mu_i$  is the chemical potential of species  $i$  [3]. Also,

$$\int = \gamma_{Sf} - \gamma_{S_0} = -\pi \quad (16)$$

$\pi$ , the spreading pressure or change in free energy, is then equal to the difference between the free surface energy of a clean, solid surface,  $\gamma_{S_0}$ , and the free surface energy,  $\gamma_{Sf}$ , of the solid when in equilibrium with a dissimilar fluid component. For a system consisting of one adsorbent and one adsorbate, the differential,  $d\pi$ , is

$$d\pi = S_{S_0} dT + \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 \quad (17)$$

If isothermal conditions are maintained and if the Gibbs plane from which adsorption is measured is chosen so the surface density of adsorbent,  $\Gamma_1$ , is zero,

$$d\pi = \Gamma_2 d\mu_2 \quad (18)$$

or

$$\Gamma_2 = \left( \frac{\partial \pi}{\partial \mu_2} \right)_{T,P,\mu_1} \quad (19)$$



If the fluid contiguous to the solid surface is a gas or vapor, the chemical potential and fugacity,  $f$ , are related by the equation

$$d\mu_2 = RT d(\ln f_2) \quad , \quad (20)$$

where  $R$  is the usual gas constant. At low pressures, the relation

$$RT d(\ln f_2) = RT d(\ln p_2)$$

is valid, and substituting,  $d\pi$  is found to be

$$d\pi = RT \Gamma_2 d(\ln p_2) \quad , \quad (21)$$

where  $p_2$  is the equilibrium pressure of the adsorbed vapor measured from zero to its saturation pressure,  $p_{o2}$ . Integration results in

$$\int_0^\pi d\pi = \gamma_{So} - \gamma_{SV} = RT \int_0^{p_2} \Gamma_2 d(\ln p_2) \quad , \quad (22)$$

where  $\gamma_{SV}$  is the free surface energy of the solid in equilibrium with the vapor.

The quantity  $\gamma_{So} - \gamma_{SV}$  is the two dimensional spreading pressure of the adsorbed film on the solid surface, or, the free energy of emersion at constant temperature of a unit surface of clean solid in an infinite amount of vapor at pressure  $p_2$ . If the solid is immersed in a saturated vapor of pressure  $p_{o2}$ , equation (22) becomes

$$\int_0^{\pi_e} d\pi = \gamma_{So} - \gamma_{Sve} = RT \int_0^{p_{o2}} \Gamma_2 d(\ln p_2) \quad , \quad (23)$$

where  $\pi_e$  is the spreading pressure at saturation, or the corresponding decrease in free surface energy, and  $\gamma_{Sve}$  is the free surface energy



of the solid in equilibrium with the saturated vapor.

The surface density,  $\Gamma_2$ , is defined as

$$\Gamma_2 = \frac{v_2}{\Sigma V} - \frac{\tau}{V_2} \quad , \quad (24)$$

where  $v_2$  is the measured adsorption,  $\Sigma$  is the specific area of the solid,  $V_2$  is the molar volume of the vapor, and  $\tau$  is the thickness of the surface region. Assuming perfect gas behavior,  $V_2 = \frac{RT}{p_2}$ , and substituting,

$$\Gamma_2 = \frac{v_2}{\Sigma V} - \frac{\tau}{RT} \quad . \quad (25)$$

Equation (23) then becomes

$$\pi_e = \frac{RT}{V_2 \Sigma} \left[ \int_0^{p_{o2}} v \, d(\ln p_2) \right] - \left[ \int_0^{p_{o2}} \tau \, dp_2 \right] \quad . \quad (26)$$

The second term makes no significant contribution and may be neglected.

The expression for free energy is then

$$\pi_e = \frac{RT}{V \Sigma} \int_0^{p_{o2}} v \, d(\ln p_2) \quad . \quad (27)$$

For decreases in free energy at pressures less than saturation the equation is given as

$$\pi = \frac{RT}{V \Sigma} \int_0^{p_2} v \, d(\ln p_2) \quad . \quad (28)$$

The evaluation of the equation requires the simultaneous determination of the volume of material adsorbed and the equilibrium pressure of the adsorbed material. Volumetric methods in use are described by Harkins [1] and others [3] and [7].



## NATURE OF PHYSICAL ADSORPTION

When a molecule of a liquid or vapor is attracted to the surface of a solid, the result is that they are more or less loosely bound together with the liberation of energy. While it is realized that the forces involved are no different from other forces which bind liquids and solids individually and cause deviations from ideal gas behavior, they will be treated as a summation of distinct forces to better correlate the theoretical approach with experimental data. Furthermore, it should be realized that little is known of the real nature of the surface itself and of the repulsive forces which oppose the attractive forces at short distances. In addition, little is known of the equilibrium distance between the surface and the molecules [2, 16].

### The Surface

It cannot be assumed that the surface of a crystalline adsorbent is a smooth two-dimensional network of atoms or ions with the same geometrical arrangement found inside the crystal. The surface ions are not symmetrically surrounded and it is generally believed from theoretical considerations that the positive ions would be found slightly inside the crystal leaving a surface of negative ions displaced outward. Since powdered solids have been used for experimental work, other disturbances of the surface result in "active spots". Among these disturbances are impurities which collect at the surfaces or at grain boundaries, remnants



of crystal faces, edges and corners, ridges, crevices, cavities, etc.

Protrusions provide the solid atoms or ions with less neighbors and they are freer to enter into a chemical bond with an adsorbed molecule. Physical adsorption, however, is not concerned with the formation of chemical bonds. Consequently, the "active spots" for physical adsorption are the crevices, cavities, insides of cracks, and capillaries where an adsorbed molecule can get into contact with more atoms of the adsorbent. Impurities, too, are important. An ionic impurity could markedly increase the heat of adsorption if polar adsorbates are used. The first molecules to be adsorbed on the surface will, therefore, often show a high adsorption energy.

### Repulsive Forces

Whatever the nature of attraction forces between molecules or atoms may be, they are checked by repulsion forces. The repulsion forces arise from the impenetrability of the electron clouds and they balance the attractive forces when the atoms are at equilibrium distance.

The expression,

$$E_{\text{rep}} = \frac{b}{r^n} \quad , \quad (29)$$

is usually used to represent the repulsion forces where  $b$  and  $n$  are constants, and  $r$  is the distance between atoms.  $n$  varies from 9 for hydrogen to 100 for carbon dioxide, and seems to be dependent upon the number of electrons in both adsorbent and adsorbate.



## Attractive Forces

These forces commonly called van der Waals' forces include all those which require no exchange or sharing of electrons. Nonpolar and polar van der Waals' forces are usually considered separately to describe the adsorption of nonpolar and polar molecules, respectively.

Nonpolar forces result from the polarization of one of the molecules participating in adsorption by the other molecule, atom, or surface. The general expression for the van der Waals' energy of interaction between two unlike atoms has been developed:

$$E_w = \frac{N_v}{4 r^3} \alpha_1 \alpha_2 \frac{I_1 I_2}{I_1 + I_2} , \quad (30)$$

where  $N_v$  is the number of atoms per  $\text{cm}^3$  in the surface,  $\alpha_1$  and  $\alpha_2$  are polarizabilities of the adsorbate and adsorbent,  $I_1$  and  $I_2$  are the corresponding ionization energies, and  $r$  is the distance from the adsorbed molecules to the surface. This energy is used to explain the adsorption of hydrocarbons on ionic surfaces and polar molecules on hydrophobic surfaces.

If the adsorbed molecule has a permanent dipole it is attracted strongly to the surface of ionic crystals. The forces involved are called polar van der Waals' forces, and when the dipole is situated such that it may come into close proximity to the surface, significantly high contributions to the adsorption energy is experienced. If the positive end of the dipole is close to the end of a molecule, the molecule will take an oriented position perpendicular to the surface. This



type of bonding is often called "hydrogen bonding" when hydrogen is the positive atom concerned and negative ions form the outer layer of the surface.

When the electrostatic field of the surface is denoted by  $F$  and the polar molecule has a dipole moment,  $\mu$ , the energy contribution is given by

$$E_{\mu} = - F \mu \quad . \quad (31)$$

When the polar molecules have dipoles of nonperipheral character, limited orientation will take place and nonpolar van der Waals' forces are dominant.

Occasionally the polarization of the adsorbed molecule will also make a contribution to the adsorption energy. This contribution is usually small but has been found to be described by the equation

$$E_{\alpha} = - F\alpha^2/2 \quad (32)$$

where  $F$  is the electrostatic field of the surface and  $\alpha$  is the polarizability of the adsorbed molecules. The energy contributions of electrostatic polarization of the adsorbed molecules are far more important on "active spots", and on projections or points of lattice disturbances may exceed the contributions of nonpolar van der Waals' forces.

Any adsorption phenomenon is a result of the cooperation of at least one of the attraction forces and repulsion forces. The nonpolar van der Waals' forces are always present and other forces may add



significant contributions. Such forces are considered additive and the mutual interaction between adjacent adsorbed molecules is considered separately. The contribution due to interaction between adsorbed molecules may also be significant in some cases; particularly after monolayer coverage would such interaction come into play.



## LITERATURE DATA

The current literature was searched for adsorption isotherms of vapors adsorbed on hydrophilic solids. These isotherms were used to evaluate the decrease in free energy by an integration of equations (28). Graphical integration was employed from zero to saturation pressure. The values determined are presented in the Appendix, Table I, and are designated  $\pi_e$ . The decrease in free energy at monolayer coverage is presented in the Appendix, Table II. While the pressure at which monolayer films form is different for different systems it is fairly well established that a relative pressure of 0.1 is a reasonable value for monolayer coverage.\* The values calculated at a relative pressure of 0.1 are designated  $\pi$ . Free energy decreases for several vapors adsorbed on mercury are presented in the Appendix, Table III. These values were obtained from surface tension measurements [6]. Selected heats of wetting are presented for comparison in the Appendix, Table IV.

It may be seen from equation (28),

$$\pi_e = \frac{RT}{V\Sigma} \int_0^{p_{o2}} v d(\ln p_2) ,$$

that accurate values of  $\pi_e$  require accurate values for the volume

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\* Relative pressure is the ratio of actual pressure,  $p_2$ , to the saturation pressure,  $p_{o2}$ .



adsorbed at low pressures. The lack of such low pressure data constitutes a serious source of error in the calculations presented here. Another source of error occurs at high pressures where the equation must be extrapolated to saturation pressure. Some analytical expressions have been devised [1], but these were found unsatisfactory.



## RESULTS AND CONCLUSIONS

Before any discussion of the data is attempted, it is desirable to consider the quantities calculated. The conventional symbols established by Harkins [1] and used in the section of this report describing heats of emersion will also be used in this section. The reduction in surface energy of a solid when it is emersed from a liquid is given as  $\gamma_S - \gamma_{SL}$ , where  $\gamma_S$  is the surface free energy of the clean solid and  $\gamma_{SL}$  is the free energy of the solid-liquid interface before emersion. The corresponding Gibbs free energy term is given as  $\gamma_S - \gamma_{Sfe}$ , if consistent symbols are employed, where  $\gamma_{Sfe}$  is the surface free energy of the solid-vapor interface in equilibrium with the saturated vapor. If  $\gamma_L$  is the surface free energy of the bulk liquid,  $\gamma_{Sfe}$  is then equal to  $\gamma_{SL} + \gamma_L$ . It can be seen that the heats of wetting contain a term involving the free surface energy of the bulk liquid as well as an entropy term. In other words,  $f_e$ , the free energy of emersion is equal numerically to  $\pi_e$ , the free energy of adsorption, plus  $\gamma_L$ , the free energy of the liquid surface.

Consequently, the heat of wetting,  $h_{E(SL)}$ , can be given as

$$h_{E(SL)} = \gamma_S - \gamma_{SL} - T \left( \frac{\partial \gamma_S}{\partial T} - \frac{\partial \gamma_{SL}}{\partial T} \right)_{P, \Sigma} \quad (4)$$

or

$$h_{E(SL)} = \pi_e + \gamma_L - T \left( \frac{\partial \gamma_S}{\partial T} - \frac{\partial \gamma_{SL}}{\partial T} \right)_{P, \Sigma} \quad (29)$$



Direct methods for calculating the entropy term have not proved successful. Indirect methods based on the above equations have been developed, but sufficient data is not available for the calculation of the entropy for the systems considered here.

It would be interesting to compare  $\sigma$ ,  $\sigma_e$  and  $\frac{h}{T}(\text{SL})$  values. Unfortunately again, insufficient experimental work has been published to allow a complete comparison; however, some information can be obtained from an examination of the available data. Because of the convention established by Harkins [1], energy of emersion is discussed rather than energy of immersion which is actually measured. The difference, of course, is only in sign. Comparisons, here, are made without regard to sign since it is understood that only magnitudes are of concern and in all cases considered, wetting occurs spontaneously with a decrease in free energy.

Calorimetric measurements of heats of emersion are easier to obtain than free energy values from adsorption data and require none of the tedious graphical integration employed with adsorption isotherms. Naturally the question arises whether calorimetric data may be used in estimating the magnitude of free energy changes. It may be said that in general high heats of emersion correspond to high free energy terms, but no simple relationship can be determined from the data at hand. For example, the data of Table I will illustrate that direct correlation is limited. (This table is to be found on page 20.) It may be significant that the differences in the heats of emersion for these solids correspond more closely to the differences in free energy values at



TABLE I

Comparison of Free Energy Terms with Heat of Wetting Values  
(ergs/cm<sup>2</sup>)

	WATER			ALCOHOL		
	$\pi_e$	$\pi$	$h_E$	n-propyl $\pi_e$	n-butyl $\pi$	$h_E$
BaSO <sub>4</sub>	246	66	490	77	50	360
SnO <sub>2</sub>	220	102	680	80	75	500
TiO <sub>2</sub>	190	80	520	108	60	350

monolayer coverage rather than at saturation. Sufficient data are not available to determine if this trend is general, and poor data may be the reason for such trend as is detected.

In considering specific items of data, one may notice the values obtained when n-heptane is adsorbed by a metal and by a metal oxide. The attractive forces involved are considered to be largely nonpolar van der Waals' forces described by equation (30).

TABLE II

Free Energy Values for n-heptane Adsorbed on Various Surfaces  
(ergs/cm<sup>2</sup>)

	$\pi$	$\pi_e$	<u>Atomic Number</u>	<u>Atomic Radius</u>
Fe (reduced)	23	53	26	1.165 Å
Cu "	2	29	29	1.173
Ag "	9	37	47	1.339
Sn "	1	50	50	1.412
Pb "	15	49	82	1.533
SnO <sub>2</sub>	17	54	--	--



It may be observed that although no simple relationship exists, values generally increase with increasing atomic number and radii. If it is assumed that the polarizabilities and ionization energies of the metals are of the same order of magnitude, the forces would vary inversely as the cube of the distance separating the adsorbed molecule and the surface. From equation (29) it is seen the repulsive forces vary inversely as the distance raised to some power no less than nine. The repulsive forces should decrease more rapidly than the attractive forces as distance increases. Such would appear to be the case if an increased atomic radius of the adsorbent means that the adsorbate distance is increased; this is not unreasonable. The values for iron may be incorrect; it was shown [18] that iron could not be easily reduced to pure metallic powder and that some oxide was always present. The values for tin and tin oxide strongly point up the effect of an oxide on the surface of a metal. That the free energy values at saturation pressures for the adsorption of n-heptane are not significantly different is attributed to the belief that the adsorbed hydrocarbon molecules do not assume an oriented position but lie flat and are limited numerically regardless of their initial attractions. That the initial attractions are different is evidenced by the differences in the  $\pi$  values for monolayer coverage.

It is to be noted that adsorption of water is characterized by large values of  $\pi$  and  $\pi_e$ . The polar van der Waals' force,  $E_\mu$ , from equation (32) may be considered to describe the major force involved, but cannot be the only force.



TABLE III

Adsorption of Water and Alcohol  
(ergs/cm<sup>2</sup>)

	<u>water (<math>\mu = 1.84</math> D)</u>		<u>n-propyl alcohol (<math>\mu = 1.64</math> D)</u>	
	$\pi_e$	$\pi$	$\pi_e$	$\pi$
TiO <sub>2</sub>	190	80	108	69
SiO <sub>2</sub>	244	54	110	55
BaSO <sub>4</sub>	246	66	77	50
Sn	168	--	83	45
SnO <sub>2</sub>	220	102	117	68
Fe <sub>2</sub> O <sub>3</sub>	205	72	122	68

The effect of the characteristics of the adsorbents themselves are observed if we compare  $\pi$  and  $\pi_e$  values for alcohol and water.  $\pi$  values for water are no more than 40 percent greater than alcohol values, but  $\pi_e$  values indicate an increase of at least 100 percent. Since the second and subsequent layers or partial layers contribute to  $\pi_e$ , the large increase for water may be indicative of more water adsorbing at saturation pressure. That dipole moment is not the answer even for initial attractions is realized by a comparison of dipole moments. (See Table IV on following page.)

The higher  $\pi$  and  $\pi_e$  values for ethyl alcohol compared to propyl alcohol may be the result of a smaller, more associated molecule. However, the fact<sup>is</sup> that different values for the same systems (anatase) precludes any rigid conclusion.



TABLE IV

Adsorption on Ferric Oxide

	$\mu$ (dipole moment)	$n_e$	$\pi$
Butyl Chloride	2.12 D	54	27
Water	1.84 D	205	72
Ethyl Alcohol	1.70 D	136	61
n-Propyl Alcohol	1.64 D	122	68

On all surfaces considered, the loss in free energy for alcohol adsorption is intermediate between that of water and that of a hydrocarbon. The  $\pi$  and  $\pi_e$  values for alcohol adsorption appear to differ less than similar values for water adsorption. The alcohol molecules are polar with a hydrocarbon tail and should be oriented perpendicular to the surface with the polar groups toward the polar solids and hydrocarbon tails directed outward. These tails exhibit little attractive energy and adsorption above monolayer coverage is believed to be small compared to water. In fact, Harkins [1] states that adsorption of n-propyl alcohol on barium sulfate is monomolecular almost to saturation.

The temperature dependency and effect of chain length for initial attraction are shown by studies of mercury (Table III in Appendix). The adsorbent while metallic is actually liquid and is presumed to have a smooth, regular surface. An increase in temperature decreases the free energy evolved in adsorption, as expected. Increasing the hydrocarbon



chain length of alcohols adsorbed on mercury increases the  $\pi$  values and further adsorption indicates that subsequent layers continue this trend [9]. Saturation values are not available to compare with the adsorption of alcohols by other materials.

In summary, it may be said that  $\pi$  values at monolayer coverage seem to be more indicative of the attractive forces between a surface and a liquid rather than equilibrium  $\pi_e$  values. Evidently, too many of the characteristics of the liquid enter into the  $\pi_e$  values. Also, differences in heats of emersion more nearly correspond to differences in  $\pi$  values rather than differences in  $\pi_e$  values.



APPENDIX



TABLE I

Values of Spreading Pressure,  $\pi_e$ ,  
 Calculated from Adsorption Data at 25°C

$$(\pi_e = \text{ergs/cm}^2)$$

	Water	n-heptane	n-propyl Alcohol		Reference
Cu		33			[17]
Cu(reduced)		29			[17]
Ag		38			[17]
Ag(reduced)		37			[17]
Pb		51			[17]
Pb(reduced)		49			[17]
Fe		54	102		[14]
Fe(reduced)		53	73		[14]
TiO <sub>2</sub> - I*	214	--	85	Benzene 56	[3]
TiO <sub>2</sub> - VI*	228	--	90	Benzene 38	[3]
SiO <sub>2</sub>	244	39	110		[3]
BaSO <sub>4</sub>	246	38	77		[3]
SnO <sub>2</sub>	220	54	117		[13]
Sn	168	50	83		[13]
TiO <sub>2</sub> *	190	46	108	n-Butane 43	[12]
Fe <sub>2</sub> O <sub>3</sub>	205	Ethyl Alcohol 136	122	Butyl Chloride 54	[18]

\* anatase



TABLE II

Values of Spreading Pressure,  $\pi$ , at Monolayer

Coverage from Adsorption Data at 25°C

( $\pi$  = ergs/cm<sup>2</sup>)

	Water	n-heptane	n-propyl Alcohol	Reference
Cu		2.5		[17]
Cu(reduced)		2.0		[17]
Ag		9		[17]
Ag(reduced)		9		[17]
Pb		15		[17]
Pb(reduced)		15		[17]
Fe		23	56	[14]
Fe(reduced)		23	30	[14]
TiO <sub>2</sub> - I*	84	--	49	[3]
TiO <sub>2</sub> - VI*	89	--	52	[3]
SiO <sub>2</sub>	54	14	55	[3]
BaSO <sub>4</sub>	66	10	50	[3]
SnO <sub>2</sub>	102	17	75	[13]
Sn	--	1	45	[13]
TiO <sub>2</sub> *	80	15	69	[12]
Fe <sub>2</sub> O <sub>3</sub>	72	Ethyl Alcohol 61	68	Butyl Chloride 27

\* anatase



TABLE III

Values of Spreading Pressure,  $\pi$ ,  
at Monolayer Coverage for Mercury

( $\pi$  = cal/g-mole adsorbate)

<u>Temperature</u>	<u>Water</u>	<u>n-heptane</u>	<u>methyl alcohol</u>	<u>n-propyl alcohol</u>	<u>amylalcohol</u>	<u>Reference</u>
25°C	6847	8817	7879	8445	10506	[9]
50°C	5949	8434	7199	8248	9730	[9]

TABLE IV

Selected Values of Energy of  
Emersion,  $h_e$ , at 25°C

( $h_e$  = ergs/cm<sup>2</sup>)

	<u>Water</u>	<u>Ethyl Acetate</u>	<u>Benzene</u>	<u>Butyl Alcohol</u>	<u>Carbon Tetrachloride</u>	<u>Reference</u>
BaSO <sub>4</sub>	490	370	140	360	220	[11]
TiO <sub>2</sub> a	520	360	150	350	240	[11]
SiO <sub>2</sub>	600	460	150	420	-	[11]
SnO <sub>2</sub>	680	530	220	500	320	[11]
TiO <sub>2</sub> b	550*	-	n-heptane 144	410	n-Butyl Chloride 502	[11]

a - anatase      \* 350 later

b - rutile



## REFERENCES

1. Harkins, W. D., "The Physical Chemistry of Surface Films," Reinhold Publishing Corporation, New York, 1952.
2. DeBoer, J. H., "Advances in Colloid Science," Vol. III, Interscience Publishers, Inc., New York, 1950.
3. Boyd, G. E., and Livingston, H. K., J. Am. Chem. Soc., 64, 2383 (1942).
4. Jura, G., and Hill, T. L., J. Am. Chem. Soc., 74, 1593 (1952).
5. Basford, P. R., Harkins, W. D., and Twiss, S. B., J. Phys. Chem., 58, 307 (1954).
6. Bangham, D. H., Trans. Faraday Soc., 33, 805 (1937).
7. Hill, T. L., Emmett, P. H., and Joyner, L. G., J. Am. Chem. Soc., 73, 5102 (1951).
8. Joyner, L. G., and Emmett, P. H., J. Am. Chem. Soc., 70, 2353 (1948).
9. Kemball, C., and Rideal, E. K., Proc. Royal Soc., 187A, 53 (1946); 190A, 117 (1947).
10. Hutchinson, E., Trans. Faraday Soc., 43, 443 (1947).
11. Harkins, W. D., and Boyd, G. E., J. Am. Chem. Soc., 64, 1195 (1942).
12. Jura, G., and Harkins, W. D., J. Am. Chem. Soc., 66, 1356 (1944).
13. Loeser, E. H., Harkins, W. D., and Twiss, S. B., J. Phys. Chem., 57, 251 (1953).
14. Loeser, E. H., Harkins, W. D., and Twiss, S. B., J. Phys. Chem., 57, 591 (1953).
15. Healey, F. H., Chessick, J. J., and Zettlemyer, A. C., J. Phys. Chem., 58, 837 (1954).
16. Chessick, J. J., Zettlemyer, A. C., Healey, F. H., and Young, G. J., Can. J. Chem., 33, 251 (1955).
17. Harkins, W. D., and Loeser, E. H., J. Chem. Physics, 18, 556 (1950).
18. Fraoli, A. V., Ph.D. Dissertation, Lehigh Univ., 1956.



## BIOGRAPHY

Sigmund Abraham, Jr. was born 9 November, 1924 in Montgomery Alabama. Parents were the late Sigmund Abraham and Myrtle Harris Abraham. Upon graduation from high school, he enlisted in the U. S. Navy and after service in the Pacific Theatre during World War II, he graduated from the U. S. Naval Academy, Annapolis, Maryland in 1947. After varied duty, including participation in the Korean conflict, he graduated from the U. S. Naval Postgraduate School, Monterey, California in 1953, having completed a course in Ordnance Engineering. At the present time Mr. Abraham is a Lieutenant in the U. S. Navy, serving aboard the U.S.S. IOWA. He is married to the former Jan Virginia Spieldoch of San Francisco, California, and has one child.







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